Archaeometric Study of 17th/18th Century Painted Pottery from the Belgrade Fortress

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ABSTRACT

The chemical and mineralogical composition of ceramic bodies, glazes and pigments, as well as the firing temperatures of main groups of Austrian period painted pottery excavated at the Belgrade Fortress on the territory of Serbia, two groups of Malhornware and one group of Anabaptist faience, were determined by a combination of powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR) spectroscopy, energy dispersive X-ray fluorescence (XRF) and micro-Raman spectroscopy. Investigated pottery was uncovered in the same archaeological context and dated the end of 17th/first decade of 18th century. The obtained mineralogical and chemical composition shows the similarities between the Malhornware groups that indicate a similar production technology. Use of calcareous clay fired at temperatures in the range 850-900 °C indicates a different production technology for the Anabaptists faience. The compositional data treatment by multivariate statistical analysis reveals heterogeneity in the Anabaptist faience group of samples, suggesting potential interactions between the local potters and the Anabaptist communities.

Keywords: Pottery; Austrian period; Powder X-ray diffraction; FTIR Spectroscopy; EDXRF Spectroscopy; Multivariate statistical analysis

1. Introduction and research aims

Modern Period aesthetics, with the elements of Renaissance and Baroque art, has made its mark in pottery, lavishly coloured and decorated with nature-inspired motifs. Although the glazed pottery products of Italian (Montelupo, Savona), French (Rouen, Nevers) and Dutch (Delft) workshops are well-known for their design, painted pottery was also produced in the 17^{th}-18^{th} century in other European regions, including the Habsburg (Austrian) Monarchy. From the late Middle Ages, Central Europe and the surrounding regions have shared a similar ceramic tradition that was in many ways continued at the time of the Austrian government [1-4].

The Austrian period painted pottery style is based on the Renaissance floral design and East Persian or Turkish flower patterns. There are three main groups, which differ in colouring and ornament patterns. Two of them belong to the so-called Malhornware [5], while the third group can be classified as Anabaptist or Haban faience [6,7]. Painted pottery belonging to all three groups spread throughout the Habsburg Monarchy. However, findings from present-day Austria, Hungary, Croatia and Serbia display a higher degree of common characteristics [8-11].

Although the Austrian period pottery (including painted pottery) was mainly analysed through individual case studies [9,12-14], more detailed and broader investigations of chronology and classifications in terms of formal and morphological features of the finds have also been performed [15]. In addition, archaeological and ethnographic analyses conducted mostly in Hungary and Austria [1,2,16-18], represent solid foundations for further research and specialised pottery studies. In spite of these recent studies, the Austrian period painted pottery production technology and the localisation of workshops are at the early stages of research. There are reports on the pottery craft, techniques and technological features derived from written documents [1,19], and experimental archaeometric studies have also been initiated. So far, painted pottery analyses from only a small number of excavation sites have been reported, such as the studies of Malhornware from Upper Austria [20] and Anabaptist or Haban faience from south Moravia [21] and Hungary [22].

The investigation of the Austrian period pottery found at the Belgrade Fortress presented here is highly complementary to these studies, as the samples represent the main groups of painted pottery (Malhornware and Anabaptist) and come from a well-studied and narrowly dated archaeological context [6,12,23]. It is therefore of interest to obtain data regarding the production process, the composition of the ceramic body and the glazes, and the firing temperatures, in order to comprehend these results in the context of the previous knowledge related to the production of painted and glazed ceramics of that time. Investigated pottery samples are dated at the early 18th century when the weakening of the internal unity of the Anabaptist communities started, and some Anabaptists assimilated into the local population firstly by joining guilds and later by converting to Catholicism [24-26]. The aim of this work is to determine similarities and differences between the three groups of pottery studied in regard to production technology. On the other hand, overall features of (painted) pottery can direct to issues of craft specialization and mass production that are associated with the establishment of manufactories in the second half of the 17th century, enabling improvement of trade and consequently firmer economic and cultural ties between parts of the Austrian Empire [27,28].

In the longer term, the results of these studies will make an important contribution to the knowledge of painted ware technology and localisation of workshops in Central Europe.

2. Context and Chronology of the Finds

As a fortress in the sphere of interest of the two great empires –Austrian and Ottoman, Belgrade has suffered due to frequent armed conflicts, especially from the late 17th century and during the 18th century. For the Austrians, as for the Turks before them, Belgrade gained importance as the main border fortress, becoming the key stronghold and the strategic point for advancing into the European possessions of the Turks. In order to transform the oriental town with old-fashioned fortifications into a modern baroque fortified town, large-scale reconstructions began shortly after the 1717 Austrian capture of Belgrade [23]. The dynamic activity in the Belgrade fortress and large-scale architectural work are evidenced by numerous archaeological contexts and findings that have the characteristics of Central European craft. The best resource for the research of the Austrian period material culture in general is the so-called

blockhouse of the Belgrade Fortress (BF), a special edifice constructed in the eastern part of the Upper Town.

The blockhouse was a rectangular fortified building with loopholes on the ground floor and a spacious subterranean vaulted chamber. It was built between 1718 and 1721, and filled in shortly afterwards due to changes in the concept of the fortification. During levelling works between 1723 and 1739, the underground chamber was partly filled in, and the rest of it and the upper parts of the building were covered a little later, following the erection of the new rampart. Unfinished and filled in, the blockhouse is not depicted on maps from that time. It was discovered during the 2008-2009 archaeological excavations. The unique stratigraphy and clear context make the filling layer one of the most significant archaeological units from the Early Modern Period in general [6]. Although various archaeological items have been found, it is the pottery collection that best defines the character of that particular epoch. It contains nearly 1,000 cooking and table vessels. Painted pottery makes about a third of ca. 300 vessels of the latter group. This pottery assemblage may be regarded as "military pottery", as it was purchased especially for the Austrian garrison. It was in use for a relatively short time, from 1717 to 1739. Consequently, the pottery (or at least the majority of the finds) must have been produced before 1717, but not much earlier than the beginning of the 18th century.

3. Materials and Methods

3.1. Description of the samples

In this work, a total of 50 samples of the Austrian period painted pottery were analysed. Three main types of vessels were identified among the findings – bowls, plates and pitchers – each with distinctive design, motifs and colours (Fig. 1). Samples were classified into three groups (BF I, BF II and BF III) according to the decoration styles in the following manner:

Group BF I (18 samples) is characterised by red painted decoration on white background (Fig. 2). The group consists of conical bowls and plates, similar in profile, size, colour and decoration style. The body colour is mainly cream to pale pinkish white (5YR 8/2–5YR 8/4 and 5YR 7/6), while the reddish yellow (5YR 7/6) slip on the exterior of the vessels occurs occasionally. The interior is decorated with

bold floral patterns, sometimes combined with bird motifs, painted in red or brown and in green. In some cases, dark brown or black contours appear [9-11,16]. A small group of plates share similar general features, but with different colour schemes, painted in black, green and yellow [2]. All samples of this group contain a very thin layer of transparent glaze applied over the decoration.

This group of pottery is known as Malhornware in the German-speaking regions. It was named after a device in the form of a horn with a goose feather on top, used for pottery decoration.This decoration style was completely defined during the first half of the 17th century [2]. It corresponds to the third Kaltenberger's group of Malhornware [5]. The "red and white style" of the BF I group samples is also defined as Hungarian, as the remains of pottery workshops have been discovered near the right bank of the Danube, in Visegrád, Szekszárd and Mórágy [11,16]. Those workshops were active from the end of the 17th to the late 18th century, and their design incorporates the Turkish floral style, used by immigrant artists from Serbia and Bosnia, and the late-Anabaptist ornamental elements. Also, it includes both contrasting variations, not only red-painted motifs on white background, but also vice versa [11].

Group BF II (15 samples) includes ware with multicoloured painted decoration on brownish red background (Fig. 3). This group contains large conical plates, uniform in profile, size and decoration. The body colour is typically cream to pale pink (5YR 7/3–7.5YR 7/2), and in some cases there is the reddish-yellow (5YR 7/6–10R 5/6) slip on the exterior of the vessels. The interior decoration is organised in three horizontal sections, following the shape of the vessel. Combined linear and schematic floral motifs painted in white, light-green, red and black appear on reddish-yellow background. Typically the same patterns are repeated in two of the three sections; schematic floral motifs (mostly leaves) are combined with grid and linear patterns painted in white, black, orange red and light green on orange to brick-red background [8-10]. Glossy transparent glaze is applied over the painted decoration.

These ceramics can be attributed to the second Kaltenberger's group [5], and are characteristic of the production at the end of the 17th and the beginning of the 18th century [1].

Group BF III (17 samples) is characterised by painted decorations on glossy white background (Fig. 4). The group consists predominantly of almost identical medium-sized pitchers and some bowls. The body colour is white to very pale pink (2.5YR 8/2–5YR 7/3). At the macroscopic level certain differences in structure and colour of ceramic body are evident. Sampling was carried out in a way which ensured that all visually different specimens were included. Glossy white glaze covers both vessel surfaces. Although the dominant colour is blue, white glaze was also painted in yellow, green, purple and black tones. Whether monochrome (blue) or polychrome, the decoration is mainly floral [8,9,26,29].

The group includes pottery attributed to the communes of Anabaptists (Habans), who lived in the so-called "historical Hungary" in northwest Hungary and south Slovakia in the late 17^{th} and 18^{th} centuries [29,30]. Organised in isolated, inward-looking and self-sufficient communities, they produced pottery, including faience, for their own use [7,26,29-31]. This indicates faience production in different workshops, and potentially application of different technologies, especially as it is known that the method of pottery making was kept as a secret by the Anabaptists [32]. In contrast to the early production, later Haban design became quite simplified and stylised [7, 9,25,29,33,34]. By comparison with the Anabaptist faience of that time, West Slovak origin (and most likely the Košolna workshops) was suggested for the late-phase production pottery [6,8]. Most vessels from the BF III group have the characteristics of the late-phase production.

3.2. Analytical methods

Optical micrographs of polished cross sections of all investigated samples were recorded by Citoval 2 Binocular Stereo Microscope Carl Zeiss Jena, under magnification x25.

X-ray fluorescence spectrometry (XRF) was employed for qualitative and quantitative elemental analysis of the ceramic body, glaze and pigment of all investigated pottery shards, using an in-house developed milli-beam spot portable energy dispersive (pEDXRF) spectrometer [35]. The spectrometer consists of an air cooled X-ray tube (Oxford Instruments, Rh anode, maximum voltage 50 kV, maximum current 1 mA), a pin-hole collimator and a Si-PIN X-ray detector (6 mm^2/500 μm, Be window 12.5 μm thickness, with energy resolution of 160 eV at 5.89

keV), associated with a DSP (X123, Amptek Inc.) for spectra acquisition. Two laser pointers were used for accurate positioning of the sample in the cross-point of the incident X-ray beam and the detector axis, respectively. ADMCA software (Amptek Inc.) [36] was used for data acquisition and processing. The qualitative analyses of ceramic body were performed on polished and cleaned areas of all investigated samples. A 35 kV voltage, 800 μA current, no filter and a 180 s measuring time in air were used as experimental parameters for all measurements. Whenever possible, measurements were performed at different fractured surfaces of each sample. Each sample was measured at three different points and the average values were used for data analysis [37]. The same method was used for glazes and pigments, but the measuring time was 200 s.

Quantitative EDXRF analysis has been performed on powdered samples of ceramic body. After removing the surface layer from each pottery shard, approximately 150 mg of ceramic body was scraped and powdered in agate mortar. The samples were taken from different parts of shards (maintaining a minimal damage), thoroughly mixed and homogenised. About 100 mg of powder was compressed using benchtop single-punch tablet press Gamlen D series Dynamic Powder Compaction Analyzer (Gamlen Instruments Ltd. Biocity Nottingham, UK). Samples were compressed at a load of 500 kg with a flat punch of 6 mm in diameter and compression speed of 60 mm/minute. The EDXRF analyses were performed under the same measuring conditions as stated for shard samples. The quantification of the obtained results was done using certified reference material (CRM): ISE sample 952 of Clay from Patjuli/Africa (Wageningen University), prepared and analysed in the same way as ceramic samples. The XRF-FP QUANTITATIVE ANALYSIS SOFTWARE (Amptek Inc.) using fundamental parameters method has been used to calculate the concentrations of the elements in the samples. The IAEA ancient Chinese ceramic (IAEA-CU-2006-06) has been used as a reference material to demonstrate the accuracy of the quantification procedure and obtained results.

The quantified values of the ceramic body composition were analyzed using One Way ANOVA analysis to detect statistically significant differences between the groups.

Ceramic samples were investigated as powders by Fourier transform infrared (FTIR) spectroscopy and powder X-ray diffraction (PXRD). Powder X-ray diffraction data were collected for samples from groups BF I and BF III on a Siemens D5000

instrument using Cu K_α radiation, in a 5-90º 2θ range, with a step size of 0.02º and a step time of 5 s. Initial phase identification was performed using the search-match routines against the PDF database [38], and the diffraction data were then analysed by the Rietveld fitting method [39] using Topas Academic software [40].

FTIR spectra of all investigated ceramic samples were recorded on a Nicolet 6700 spectrophotometer, using KBr pellets technique in the wavenumber range from 4000 cm^{-1} to 400 cm^{-1}, with resolution of 2 cm^{-1} and 64 acquisitions. Assignation of bands in the FTIR spectra was done by comparison of the recorded spectra with those from literature [41].

Micro-Raman spectra of coloured glazes of representative samples were recorded *in situ* on a DXR Raman Microscope (Termo Scientific). The 532 nm line of a diode-pumped solid state high brightness laser was used as the exciting radiation and the power of illumination at the sample surface was 10 mW. Collection of the scattered light was made through an Olympus microscope with infinity-corrected confocal optics, 50 μm pinhole aperture, standard working distance objective 10×, grating of 900 lines/mm, and resolution of 2 cm^{-1}. Acquisition time was 10 s with 10 scans. Thermo Scientific OMNIC software was used for spectra collection and manipulation. The identification of pigments was performed by comparison of the recorded spectra with those from our inhouse database and the literature [37].

3.3. Multivariate statistical analysis

The results of elemental analysis (obtained by pEDXRF) of the ceramics were used to form multivariate datasets in the form of a 50×12 matrix. For each sample the average value of three measurements for the Net Peak Area parameter was evaluated for selected elements [37]. An element was considered to be present if its Net Peak Area uncertainty was below 10 % (Cr and Cu did not satisfy this condition and were excluded from analysis). The data in the datasets were autoscaled prior to PCA analysis [43].

Principal component analysis (PCA) and the scattering matrix based dimension reduction were applied as unsupervised and supervised pattern recognition technique, respectively, to explore the grouping and classification of the pottery samples [44,45]. The aim of the PCA analysis was to extract the parameters carrying the majority of variability, which may consequently structure the initial dataset into

several groups. The scattering matrix based dimension reduction, supported by the Bhattacharyya distance evaluation, was carried out to test the initial archaeological classification of the shards [46]. Multivariate analyses were performed in MATLAB - version R2010a, Math Works, Inc. environment and IBM SPSS Statistics 19, software package.

4. Results and Discussion

4.1. Chemical and mineralogical composition of pottery

4.1.1. Microstructure

Optical micrographs of polished cross sections of representative pottery shards are given in Fig. 5.

Cross sections of samples from BF I and BF II groups are very similar in terms of quantity and size of particles. Among them BF I-2 and BF II-15 have very fine-textured fabric with grains maximum sizes from 0.2 to 0.4 mm. Voids in cross sections reaching even 1 mm in length are resulting from the release of gases due to the vitrification in the process of firing [47]. Elongated voids in BF I-5, BF I-6, BF II-6, BF II-9 indicate the air trapped in the plastic clay during the kneading and construction process; it also can be due to insufficient and improper drying of vessels [48]. Most samples have cross sections of uniform colours, however, in the case of BF I-16, BF I-17 and BF I-18 one can see slightly darker core and lighter margins; in the situation of mass production, which is the case here, the slightly darker core and lighter margins could be consequence of 'problems'/inconsistencies in firing and cooling processes (such as swift firing) [49]. Most samples in BF III group have a compact and very fine-textured fabric, with small and relatively evenly distributed voids, although the particles in BF III-6 seem slightly larger and the voids in BF III-9 appear grouped. The glaze thickness varies from sample to sample as well as at different locations of the same sample. Pottery samples from groups BF I and BF II have thin glaze that is approximately 150 μm thick only on one surface. Majority of samples from group BF III have glaze on both surfaces with average thickness of 300 μm; this finding is in agreement with results obtained for 17th century faience artefacts found in Hungary [22]. Optical micrographs of cross sections of all investigated pottery samples are given in Table S1 (in Supplementary Material).

4.1.2. EDXRF spectroscopy

The following elements were identified in the EDXRF spectra of ceramic body of all investigated samples: Si, K, Ca, Ti, Mn, Fe, Zn, Pb, Rb, Sr, Y and Zr. The quantified values of the ceramic body composition are presented in the Table 1. Some elements (Si, K, Ca, Ti, Mn, Fe) are presented in their oxide percentage taking into account the composition of CRM used for calibration, while the minor elements (Zn, Pb, Rb, Sr, Y and Zr) are reported in ppm. The results of one-way analysis of variance (ANOVA) is presented in Table S2 (in Supplementary Material). Most of the elements show significant p values, ranging from 0.018 for Fe_2O_3 and 0.013 for Sr to lowest calculated values for SiO_2, CaO, TiO_2, MnO, Rb and Zr (Table S2), indicating that between-group difference exists.

The small amount of CaO and high SiO_2 content detected for samples from groups BF I and BF II reveal that the clays represented in analysed shards are non-calcareous. Also, mean values of CaO content for samples from groups BF I and BF II are similar. However, lower SiO_2 content and higher CaO content indicate that samples from group BF III were made of calcareous clays. The samples BF III-6 and BF III-14 have lower CaO content (< 5 %) and higher SiO_2 content compared to the other samples in group BF III.

4.1.3. PXRD analysis

Representative PXRD patterns and the Rietveld fits obtained are shown in Fig. 6. Patterns of all samples are dominated by reflections of quartz. In addition, BF I samples contain illite group phyllosilicates (muscovite, illite) and plagioclase group of feldspars (anorthite, andesine) (Fig. 6a-b), while the presence of higher temperature phases (diopside, gehlenite) is typical for most BF III samples (Fig. 6c-d). A notable exception is sample BF III-15 (Fig. 6e), whose PXRD pattern clearly resembles those of the BF I group. Also, mineralogical composition of sample BF III-14differs from the rest of BF III group and is similar to the composition of BF I group. Mineral composition of all samples from groups BF I and BF III determined by PXRD is given in Table S3 (in Supplementary material).

The mineralogical phase content obtained from the PXRD data analysis can be used to estimate the firing temperature used in the production of the investigated

pottery. Gehlenite forms from the decomposition products of illite and calcite at 800-850 ^{o}C [50,51], while diopside is obtained from illite, calcite and quartz at 850-900 ^{o}C [52]. The presence of these phases in the BF III samples (exemplified by the intense features between 35-37^{o} 2θ) therefore indicates a firing temperature of about 850-900 ^{o}C. Also, presence of gehlenite can indicate inhomogeneous and coarser grained calcite in the source material [53]. The BF I samples have simple mineralogical content, but the presence of muscovite and illite in this group suggests that the firing temperature did not exceed 900 ^{o}C, because phyllosilicates disappear at temperatures between 900 and 950 ^{o}C [54]. Samples BF III-14 and BF III-15 display a PXRD pattern dissimilar to the rest of this group, and their mineralogical content (quartz, muscovite, illite, andesine) suggests that these samples belong to the BF I group of artefacts.

Calcite is absent in the BF I PXRD patterns, but it is detected in six of the BF III samples. Results obtained for Anabaptist 17th century ceramic artefacts found in Hungary [22] show similar mineralogical compostion to group BF III. This result is particularly important in the wider context, due to the constancy of some manufacturing sequences, especially the strategy of procurement of raw materials and firing procedures in all chronological stages of production of Haban faience.

4.1.4. FTIR Spectroscopy

The FTIR spectra representative of each group of the Belgrade Fortress pottery in the range of 2000 – 400 cm^{-1} are shown at Fig. 7.

FTIR spectra of BF I and BF II samples show very similar features and are dominated by a broad band in the range 1250 – 900 cm^{-1}. This strong band originates from the Si-O stretching vibrations of various silicate minerals. When raw clay material is fired, some minerals undergo structural changes or destruction while new ones are formed; hence the mineralogical composition of the pottery can be related to the firing temperature. Since FTIR spectroscopy is a technique sensitive to local structure, this band is influenced by structural changes in the clay material and the maximum of the Si-O stretching band changes with firing temperature [55-57]. Most (24 out of 32) samples from groups BF I and BF II have a maximum of the Si-O band at about 1085 cm^{-1}, indicating similar firing temperature for these samples. In the FTIR spectra of three samples (BF I-7, BF I-11 and BF I-16) this band is split and has

two maxima at 1083 cm^{-1} and 1046 cm^{-1}, while in the case of five samples it is shifted to lower wavenumbers: 1052 cm^{-1} for BF II-7, 1054 cm^{-1} for BF II-4, 1065 cm^{-1} for BF II-2, 1071 $cm^{-1}$for BF II-6 and 1075 cm^{-1} for BF II-5.

The Si-O stretching band has a significantly different structure in the FTIR spectra of group BF III samples. For 15 of 17 of them, the Si-O stretching band contains shoulders suggesting contributions from a larger number of silicate minerals, Fig. 7. The maximum intensity of this structured band is at about 1060 cm^{-1} for 9 samples (BF III-1, BF III-3, BF III-4, BF III-5, BF III-6, BF III-7, BF III-11, BF III-16, BF III-17) and for samples BF III-9, BF III -10 and BF III-12 it is at 1070 cm^{-1}. For samples BF III-2 and BF III-8 maximum it is at 1040 cm^{-1}, while for BF III-13 it is at 1030 cm^{-1}. The maxima of the other two peaks that contribute to the Si-O stretching band are at about 970 cm^{-1} and 925 cm^{-1} for all samples from BF III group.

FTIR spectra of samples BF III-14 and BF III-15 are very different from the rest of group (see Fig. 7), featuring Si-O stretching bands with a single maximum at 1085 cm^{-1}, similar to those observed in FTIR spectra obtained for groups BF I and BF II. This finding is in perfect agreement with PXRD results showing that mineralogical composition of these two samples resembles group BF I.

It has been shown that position of the maximum of the Si-O band shifts towards higher values of wavenumbers with increasing firing temperature [55-57]. It allows conclusion that firing temperature for samples for group BF III (except for samples BF III-14 and BF III-15) was lower compared to pottery from groups BF I and BF II, which is in agreement with PXRD results.

Calcite is identified in 17 pottery samples from groups BF II and BF III by characteristic peaks at 1430 and 875 cm^{-1} [41]. These samples are: BF II-3, BF II-5, BF II-6, BF II-7, BF II-9, BF II-11, BF II-12, BF II-14, BF III-1, BF III-2, BF III-3, BF III-4, BF III-6, BF III-7, BF III-8, BF III-10, BF III-12 and BF III-13. Comparing FTIR and PXRD data for samples from group BF III it is obvious that calcite was not detected in the same samples. Possible reasons for this inconsistency are presence of calcite bellow PXRD detection limit, poor crystallinity or small particle size in particular samples. However, calcite was not detected in FTIR spectra of samples from group BF I. This is consistent with the XRPD findings.

4.1.5. Statistical treatment of chemical composition data

The difference between samples in the initial dataset can be seen in the space of maximal variance obtained by PCA dimension reduction of the 50x12 dataset into three dimensional space of maximal variance (Fig. 8a). The first three principal components account 71 % of the total variance in this dataset, indicating that some of information was lost by data selection. Fig. 8b shows that group BF III is highly incoherent, but clearly separated from the other two groups.

However, one sample (BF III-15) appears to show the characteristics of other two groups. Furthermore, samples which were assigned by archaeologists to groups BF I and BF II cannot be distinguished as different groups by this PCA analysis, indicating similar elemental composition (possibly similar clay material). Data that carry information about the variability in the dataset were extracted during dimension reduction. Elements such as Ti, Zr, Ca and Pb have high loading values (Fig. 8b) and are therefore elements of important variability. Additional Post-hoc Tukey's Honestly Significant Differences test was used to evaluate each pair-wise comparison for the presence of significant differences. The obtained results presented in Table S4 (in Supplementary material) show very good agreement in the significance determined by ANOVA analysis with variables (carrying information about variability in dataset) extracted during dimension reduction by PCA. The variance of CaO is the parameter most responsible for significant separability of ceramic shards from the BF III group indicating usage of raw material or preparation technique different than the one used for production of ceramics grouped to BF I and BF II. The smallest p-values for SiO_2, TiO_2, Fe_2O_3, Rb and Y could indicate that the source of separability between ceramic belongs to BF I and BF II groups.

Since the PCA analysis did not completely support initial archaeological grouping of the samples (between group distances in space of maximal variance is not sufficient high for classification), and to investigate the possibility of differentiating groups BF I and BF II, scattering matrix based dimension reduction was performed on a 50×12 dataset of pEDXRF data. The obtained result is shown in Fig. 9.

The separability between groups can be measured by the Bhattacharyya distance, $\mu(1/2)$. The value of this parameter of 6.5 between BF III and the others, indicates good separability between these groups. However, group BF III is notably incoherent, which indicates additional structuring in this group. The same trend in

production is determined for material from Strachotín, Břeclav district where at least two groups are identified based on structure and colour of ceramic body [58]

The value of the Bhattacharyya distance of 4.3 between groups BF I and BF II is also sufficiently large for classification purposes [59]. These two groups appear well-separated, and the sample BF III-15, visually similar to the Haban faience, shows compositional characteristics of the BF I group.

4.2. Composition of glaze and pigments in decorative glazed coatings

EDXRF and micro-Raman analyses of pigments were performed on representative shards, with characteristically coloured details and the pigmented areas suitable for measurements. The EDXRF spectra were collected on glazed spots both with and without pigmented decoration.

EDXRF analyses of the glazes, collected at well-preserved spots away from the pigmented areas, identified the same elemental composition for groups BF I and BF II. The spectra reveal the presence of Pb and K as the main constituents, pointing to a PbO-based glaze in all fragments, where lead represents a flux agent. The main difference between EDXRF spectra of glazes of three investigated groups is the presence of Sn in the EDXRF spectra of BF III group (see Fig. S1. in Supplementary Material). It is well known that opacification of the glaze is achieved by addition of tin oxide (SnO_2) [60,61]. A comparison of the EDXRF spectra suggests that the lead oxide-based glaze used for group BFIII contained significantly more tin-oxide than appears to be the case for groups BF I and BF II. This conclusion is consistent with the PXRD patterns recorded on the glazes (see Fig. S2. in Supplementary Material). Moreover, ceramic body of samples from group BF III is made of calcareous clays, as shown by presented results of chemical and mineralogical composition, which is typical for tin-glazed maiolica pottery [60]. When the body is made of calcareous clay a white glaze is achieved at lower concentrations of tin oxide than in the case of red non-calcareous body [62]. Also, such bodies have higher thermal expansion coefficient than non-calcareous clays which is similar to those of lead-alkali glazes preventing glaze crazing during the cooling [60,62].

The presence of Fe and Mn at dark brown decorations, identified in EDXRF spectra of samples from groups BF I and BF II, indicate use of earth pigments, most likely umber (iron oxide with 6-15 % of MnO_2 + clay + silica) [63]. In the case of light brown decorations of pottery from groups BF I and BF II, EDXRF analysis did

not show presence of Mn, and Raman spectrum shows typical signature of hematite at 223, 243, 291, 405, 496, 611 and the strong mode at 1316 cm^{-1} assigned to a two-magnon scattering band [64], Fig 10a. Hematite is the chromophore of red natural pigments such as red ochre (Fe_2O_3 + clay + silica). Doublet at 611 and 660 cm^{-1} is characteristic for red pigments (red ochre and earths) where the first band originates from hematite and the second from magnetite which is responsible for darker shades of red colour [64]. Broad band at 960 cm^{-1} originates from stretching Si-O vibrations of glassy matrix and confirms that glazes have lead-based composition [65].

EDXRF analyses identified the use of copper at green decorations of the BF I and BF II shards. Raman signature specific for green pigments was not detected, which is in agreement with the use of Cu^{2+} ions dispersed in the glassy matrix for green decorations [66].

Cobalt, arsenic, nickel and iron were identified at blue pigmented parts of glazed decorations of samples from BFIII group by the EDXRF analysis. The blue colour of glaze can be obtained by dissolution of Co^{2+} ions in the glassy phase during firing. When Co^{2+} ions concentration is higher than a few weight percent Co-silicate or Co-aluminate compounds precipitate and can be revealed in the glaze [67]. The very strong Raman band at 824 cm^{-1} with large bandwidth is detected in the micro-Raman spectrum of blue glaze of samples from group BF III, Fig. 10b. Raman signature of Co-silicate with olivine structure (Co_2SiO_4) appears in the same wavenumber range, but it is a doublet with much narrower bandwidth [68]. However, arsenate-based compounds show strong band originating from As-O stretching vibrations between 800 and 830 cm^{-1} [67,68]. Hence, this result allows identification of lead arsenate in the blue glaze. Also, this finding indicates origin of the cobalt ore used for blue pigment because the lead arsenate is formed from the content of arsenic in cobalt ores originating from the Erzgebirge mining region in Saxony and exploited from the 16th to the 18th century [67-70]. The quartz is identified by the band at 463 cm^{-1} and Raman band at ~990 cm^{-1} originates from the envelope of Si-O stretching bonds from the glaze [71].

The absence of the peaks of the other characteristic elements and the detection of the Pb, Sn and Sb peaks in the EDXRF spectra collected at the yellow parts of the glazed surface of fragment BF III-7, indicate the use of lead(II) antimonate or lead tin yellow pigments. However, since Sn is also present in the glaze as the opacifier (SnO_2) XRF analysis alone cannot unambiguously identify the yellow pigment used.

Results obtained by the non-invasive micro-Raman analysis show (Fig. 11) an intense band at 126 cm^{-1} along with the peaks at 302, 338, 390, 461 and 511 cm^{-1} indicating the presence of pyrochlore-type Sn-containing lead(II) antimonate ($Pb_2Sb_{2-x}Sn_xO_{7-x/2}$) [72,73]. Band at 659 cm^{-1} originates from small amounts of rosiaite ($PbSb_2O_6$) which can be found in yellow lead antimonate pigments on ancient ceramics [74].

Lead antimonate yellow ($Pb_2Sb_2O_7$) is one of the oldest synthetic pigments used in Egypt and Mesopotamia from 16^{th}-14^{th} century B.C. [73]. Since the end of 17^{th} century it has been known as Naples Yellow. This pigment has been commonly used in maiolica ceramics since the late 14^{th} century and in European oil painting (since 16^{th} century) [66], but it was also identified in 12^{th}-14^{th} century Byzantine ceramics [65,75]. Lead antimonite adopts a pyrochlore-type structure. Pyrochlores have the general formula $A_2B_2O_7$, and while the ideal pyrochlore structure is cubic, several lower-symmetry distorted variants of the structure exist [76]. The pyrochlore structure can accommodate cations in different combinations of oxidation states, with the A cation in scalenohedral and the B cation in trigonal antiprismatic coordination environment. Consequently, different modifications of lead antimonate yellow pigment have been made through history, depending on the availability of raw material and the technological knowledge, in order to achieve different hues of yellow [65,73]. Presence of different cations in pyrochlore structure is evident in shifts of signals in Raman spectra [73]. Tin-lead antimonate has been identified in 16^{th} century Italian maiolica [73,77] and in 17^{th} century paintings [78] and it can be considered as one of production markers for period 16^{th} and 17^{th} century. This coincides with characteristics of Renaissance Italian maiolica and it is known that Haban faience production is based on Renaissance Italian maiolica production technology [22,32].

5. Conclusions

The multianalytical study of Austrian period painted pottery (50 samples) excavated at the Belgrade Fortress on the territory of Serbia allowed determination of the chemical and mineralogical composition of the body, glaze, pigments, and the firing temperature. Investigated samples include three main groups of painted pottery: Malhornware (BF I and BF II) and Anabaptists faience (BF III). Because of the clearly defined archaeological context, pottery is securely dated at the end of 17^{th}/first decade of 18^{th} century. The mineral assemblage determined by PXRD and FTIR spectroscopy, as well as chemical composition of body and glaze determined by

EDXRF spectroscopy, show significant similarities between groups BF I and BF II indicating that these groups are likely to originate from a similar production technology. This finding can imply modernisation and standardisation in pottery production in Early Modern Period [27,28]. Results obtained for group BF III support a different production technology, typical for Anabaptists communities (use of calcareous clay, firing temperature about 850-900 ^{o}C, use of tin oxide as glaze opacifier, use of pigments such as Sn-containing lead(II) antimonate). In addition, the heterogeneity within group BF III observed by statistical treatment of compositional data and the close similarity of chemical and mineralogical composition of one sample from this group to the other two groups may suggest that Anabaptists interacted with local potters in the late-phase, i.e. at the beginning of the 18th century. Having in mind transformation of Anabaptist communities in the early18th century, these findings indicate the need for further research on the interactions between the local potters and the Anabaptist communities in Central Europe.

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References

[1] A. Kaltenberger, Keramik des Mittelalters und der Neuzeit in Oberösterreich, Band 1: Grundlagen. Studien zur Kulturgeschichte von Oberösterreich 23 – NEARCHOS Band 17. Innsbruck: Bibliothek der Provinz, 2007.

[2] A. Kaltenberger, Keramik des Mittelalters und der Neuzeit in Oberösterreich, Band 2: Katalog. Studien zur Kulturgeschichte von Oberösterreich 24 – NEARCHOS Band 18. Innsbruck: Bibliothek der Provinz, 2007.

[3] V. Pacher, S. Sabeditsch, Die mittelalterlichen und neuezeitlichen Funde und Befunde der Grabung Krems/Bundeskonvikt 2007, In: Keramik und Technik. Internationale Fachtagung der ÖGM. 43. Internationales Symposium Keramikforschung, Mautern an der Donau, September 2010, S. Herausgegeben von Felgenhauer-Schmiedt, N. Hofer, K. Kühtreiber, G. Scharrer-Liüka, Beiträge zür Mittelalterachäologie in Österreich 27, 2011, pp. 314-333.

[4] H. Steininger, Die münzdatierte Keramik in Österreich, 12. bis 18. Jahrhundert, Fundkatalog. Wien: VWGÖ, 1985.

[5] A. Kaltenberger, Die Grabungen des Österreichischen Archäologischen Institut im ehem. Benediktinerkloster ("Schloss") Mondsee. III. Die frühneuzeitliche Malhornware. *Jahrbuch* des Oberösterreichischen Musealvereines 141/I, 1996, pp. 187-227.

[6] V. Bikić, The Haban Pottery from the Belgrade Fortress: Archaeological Contexts, Chronology, Decorative Designs, Starinar LXII (2012) 205-227.

[7] A. Ridovics, A habánkerámia a 17. században (Haban ceramics in the 17th century), In: Á. Mikó, (Ed.), Mátyáskirályörököse. Későreneszánszművészet Magyarországon (16-17. század), vol. II. Publication of the Hungarian National Gallery, Budapest, 2008, pp. 86-97.

[8] M. Bajalović-Hadži-Pešić, Nalazi habanske i posthabanske keramike u Srbiji, Godišnjak grada Beograda XLVII-XLVIII/2000-2001, 2001, pp. 107-121.

[9] I. Horvat, R. Biondić, Keramika i staklo 17. i 18. stoljeća iz starog franjevačkog manastira, Katalog izložbe. Osijek: Muzej Slavonije, 2007.

[10] M. Krenn, J. Kraschitzer, D. Schön, J. Wagner, Koch- und Taferlgeschirr des 18. Jahrhunderts, Ein Keramikfunkomplex aus Melk, Niederösterreich. Fundberichte aus Österreich Materialheft A 17. Wien, 2007.

[11] G. Mésárosz, Szekszárd és környéke törökös díszítésű kerámiai emlékei, Szekszárd, 1968.

[12] V. Bikić, Gradska keramika Beograda (16-17. vek), Posebna izdanja 39. Beograd: Arheološki institut, 2003.
[13] Z. Himmelova, R. Procházka, On the characteristic of some components of material culture and public health care of the town Brno in the 16th-17th century, In: Z. Smetánka, J. Žegklitz, (Eds.), Studies in postmediaeval archaeology 1, Prague: Archaeological Institute of Czechoslovak Academy of Science, 1990, pp. 127-162.
[14] G. Kovács, Ceramic finds from the Bajcsa fort (1578-1600), Acta Arch. Hung. 52 (2001) 195-221.
[15] N. Hofer (Schriftleitung), Handbuch zur Terminologie der mitelalterlichen und neuezeitlichen Keramik in Österreich, Fundberichte aus Österreich Materialhefte. Wien: Österreichische Gesellschaft für Mittelarchäologie, 2010.
[16] G. Kovács, 16th-18th century Hungarian pottery types, Antaeus 19-20 (1990-1991) 169-180.
[17] O. Lajkó, A kora újkori kerámia tipológiája – a néprajzi edényterminológia alkalmazásának lehetőségei a dél-alföldön, In: E. Benkő, G. Kovács, (Eds.), Archaeology of the Middle Ages and the Early Modern Period in Hungary. II. Budapest: Archaeological institute of the Hungarian Academy of Science, 2010, pp. 799-816.
[18] M. Vizi, A kora újkori kerámia feldolgozásának módszerei. Az Ozorai várkastély leletanyagának adatbázisáról, In: E. Benkő, G. Kovács, (Eds.), Archaeology of the Middle Ages and the Early Modern Period in Hungary. II. Budapest: Archaeological institute of the Hungarian Academy of Science, 2010, pp. 817-838.
[19] U. Mämpel, Die technische Überwindung der giftigen Bleiglasur, In: Keramik und Technik. Internationale Fachtagung der ÖGM. 43. Internationales Symposium Keramikforschung, Mautern an der Donau, September 2010, S. Herausgegeben von Felgenhauer-Schmiedt, N. Hofer, K. Kühtreiber, G. Scharrer-Liüka, Beiträge zür Mittelalterachäologie in Österreich 27, 2011, pp.199-204.
[20] R. Sauer, Ergebnisse der petrographischen Dünnschliff- und Schwermineralanlysen, In: A. Kaltenbeerger, (Ed.), Keramik des Mittelalters und der Neuzeit in Oberösterreich. Band 2: Katalog. Studienzur Kulturgeschichte von Oberösterreich 24 – NEARCHOS Band 18. Innsbruck: Bibliothek der Provinz, 2007, pp. 7-89.

[21] T. Trojek, M. Hlozek, T. Cechak, L. Musílek, X-ray fluorescence analysers for investigating postmedieval pottery from south Moravia, J. Archaeol. Sci. 68 (2010) 879–883.
[22] B. Bajnóczi, G. Nagy, M. Tóth, I. Ringer, A. Ridovics, Archaeometric characterization of 17th century tin-glazed Anabaptist (Hutterite) faience artefacts from North-East-Hungary, J. Archaeol. Sci. 45 (2014) 1-14.
[23] M. Popović, Beogradska tvrđava (drugo dopunjeno izdanje), Beograd: Javno preduzeće "Beogradska tvrđava", 2006.
[24] R. Friedmann, Hutterite Studies, Celebrating the Life and Work of an Anabaptist Scholar, Library and Archives Canada Cataloguing in Publication: Menonite Historical Society, 1961, pp. 152-153.
[25] J. Kybalová, J. Novotná, Habánská fajáns 1590-1730, Uméleckoprumyslové museum v Praze – Moravská galerie v Brné, Praha-Brno, 1981, pp. 25-26.
[26] L. Réti, (Ed.), Haban Myth 1593-1738, Treasures from Hungarian Private Collections, An Exhibition Catalogue. Budapest: Museum of Applied Arts, 2007, pp. 17.
[27] V. Bikić, Early Modern Period Pottery from Belgrade: Production and Consumption Models. Ceramics and its dimensions Symposium: Ceramics between change and challenge – between past and present, Belgrade, 20–21 May 2015, B. Crvenković and J, Popović, (Eds), Belgrade: Museum of Applied Arts 2016.
[28] R. Veselinović, Prodiranje austrijske trgovine u Beograd u drugoj polovini XVII veka. In: V. Čubrilović, (Ed.), Oslobođenje gradova u Srbiji od Turaka 1862-1867. god. Beograd: SANU, Odeljenje društvenih nauka, 1970, pp.163-179.
[29] J.E. Horvat, M.H. Krisztinkovich, A History of Haban Ceramics, A Private View, A Canadian Collection of Hungarica, Volume V. Vancouver BC Canada, 2005.
[30] J. Pajer, Novořtěnecké fajánse na Moravy 1593-1620, Soupis dokladů z institucionálních a privátních sbírek, Strážnice, 2011.
[31] J. Pajer, Novořtěnecké fajánse v Strachotiná, Mikulov, 2001.
[32] B. Kristinkovič, Keramika Habanov, Budapešt: Korvina (in Russian), 1962, pp. 41-46.
[33] A. Gaál, Kerámialeletek Szeksárd-palánkitörökpalánkvár (JeniPalanka) területérőlfeltásárából, Mázasasztaliedények, Wosinski Mór Museumévkönyve XXXII, 2010, 401-452.

[34] A. Kalinová, Nejstaršidokladylidové fajánsez Moravy, Foliaethnographica, Supplementumad Acta Musei Moraviae 39 (2005) 3-15.
[35] M. Gajić-Kvaščev, M. Marić-Stojanović, R. Jančić-Heinemann, G. Kvaščev, V. Andrić, Non-destructive characterisation and classification of ceramic artefacts using pEDXRF and statistical pattern recognition, Chem. Cent. J. 6 (2012)102.
[36] http://www.amptek.com/pdf/mca8000a.pdf.
[37] N. Forster, P. Grave, N. Vickery, L. Kealhofer, Non-destructive analysis using PXRF: methodology and application to archaeological ceramics, X-Ray Spectrom. 40 (2011) 389-398.
[38] Powder Diffraction Database, PDF4, International Centre for Diffraction Data, USA; http://www.icdd.com/products/pdf4.htm.
[39] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, J. Appl. Crystallogr. 2 (1969) 65-71.
[40] A.A. Coelho, J.S.O. Evans, I.R. Evans, A. Kern, S. Parsons, The TOPAS symbolic computation system, Powder Diffr. 26 (2011) S22-S25.
[41] V.C. Farmer, Infrared spectra of Minerals, Minerological Society, London, 1974.
[42] L. Burgio, R.J.H . Clark, Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation, Spectrochim. Acta Part A 57 (2001) 1491-1521.
[43] K. Varmuza, P. Filzmoser, Introduction to Multivariate Statistical Analysis in Chemometrics, CRC Press, Boca Raton FL, 2000.
[44] M.J. Baxter, A Review of Supervised and Unsupervised Pattern Recognition in Archaeometry, Archaeometry 48 (2006) 671-694.
[45] R.G. Brereton, Chemometrics Data Analysis for the Laboratory and Chemical Plant, John Wiley & Sons Ltd, Chichester, West Sussex, 2003.
[46] K. Fukunaga, Introduction to Statistical Pattern Recognition-second ed, Academic Press, Orlando, 1990.
[47] P.S. Quin, Ceramic Petrography. The Interpretation of Archaeological Pottery and Related Artefacts in Thin Section, Archaeopress: Oxford, 2013, pp. 61-68, 97-99.
[48] N.S. Müller, V. Kilikoglou, P.M. Dayb, G.Vekinis, The influence of temper shape on the mechanical properties of archaeological ceramics, J. Eur. Ceram. Soc. 30 (2010) 2457–2465.
[49] O.S. Rye, Pottery technology: principles and reconstruction, Manuals on Archaeology 4. Washington. D.C., 1981.

[50] L. Maritan, L. Nodari, C. Mazzoli, A. Milano, U. Russo, Influence of firing conditions on ceramic products: Experimental study on clay rich in organic matter, Appl. Clay Sci. 31 (2006) 1-15.
[51] M.P. Riccardi, B. Messiga, P. Duminuco, An approach to the dynamics of clay firing, Appl. Clay Sci. 15 (1999) 393-409.
[52] G. Barone, V. Crupi, S. Galli, D. Majolino, P. Migliardo, V. Venuti, Spectroscopic investigation of Greek ceramic artefacts, J. Mol. Struct. 651-653 (2003) 449-458.
[53] R. Kreimeyer, Some notes on the Firing Colour of Clay Bricks, Appl. Clay Sci. 2 (1987) 175-183.
[54] G.E. De Benedetto, R. Laviano, L. Sabbatini, P.G. Zambonin, Infrared spectroscopy in the mineralogical characterization of ancient pottery, J. Cult. Herit. 3 (2002) 177-186.
[55] Lj. Damjanović, I. Holclajtner-Antunović, U.B. Mioč, V. Bikić, D. Milovanović, I. Radosavljević Evans, Archaeometric study of medieval pottery excavated at Stari (Old) Ras, Serbia, J. Archaeol. Sci. 38 (2011) 818-828.
[56] Lj. Damjanović, V. Bikić, K. Šarić, S. Erić, I. Holclajtner-Antunović, Characterization of the early Byzantine pottery from Caričin Grad (south Serbia) in terms of composition and firing temperature, J. Archaeol. Sci. 46 (2014) 156–72.
[57] S. Shoval, The firing temperature of a Persian-period pottery kiln at Tel Mihal, Israel, estimated from the composition of its pottery, J. Therm. Anal. 42 (1994) 175-185.
[58] M. Gregerová, M. Hložek, Z. Kuljovská, Micropetrografické a petrochemicé rozbory novověké glazované keramiky z locality Srachotín (Micropetrographic and Petrochemical Analyses of Postmedieval Pottery from Strachotín). In: Geol. výzk. Mor. Slez. v r. 2006, Brno 2007, pp. 95-100.
[59] L. Stepanic, I.V. Latinovic, Z. Djurovic, A new approach to detection of defects in rolling element bearings based on statistical pattern recognition, Int. J. Adv. Manuf. Technol. 45 (2009) 91–100.
[60] M.S. Tite, The production technology of Italian maiolica: a reassessment, J. Archaeol. Sci. 36 (2009) 2065–2080.
[61] M. Tite, T. Pradell and A. Shortland, Discovery, production and use of tin-based opacifiers in glasses, enamels and glazes from the Late Iron Age onwards: a reassessment, Archaeometry 50 (2008) 67-84.

[62] M.S.Tite, I. Freestone, R. Mason, J. Molera, M. Vendrell-Saz, N. Wood, Lead glazes in antiquity – methods of production and reasons for use, Archaeometry 40 (1998) 241–60.
[63] N. Bevilacqua, L. Borgioli, I. Adrover Gracia, In: M. Matteini, (Ed.), I Pigmenti-nell'arte. Dalla Preistoria Alla Rivoluzione Industrilae. Il Prato, Saonara, Italy, 2010.
[64] F. Froment, A. Tournié, P. Colomban, Raman identification of natural red to yellow pigments: ochre and iron-containing ores, J. Raman Spectrosc. 39 (2008) 560-568.
[65] B.B. Kirmizi, E.H. Göktürk, P. Colomban, Colouring agents in the pottery glazes of western Anatolia: new evidences for the use of naples yellow pigment variations during the late Byzantine period, Archaeometry 57 (2015) 476-496.
[66] P. Colomban, L. Arberet, B. Kirmizi, On-Site Raman Analysis of 17th and 18th Century Limoges Enamels: Implications on the European Cobalt Sources and the Technological Relationship Between Limoges and Chinese Enamels, Ceram. Int. 43 (2017) 10158-10165.
[67] P. Colomban, Y. Zhang, B. Zhao, Non-invasive Raman analyses of Chinese huafalang and related porcelain wares. Searching for evidence for innovative pigment technologies, Ceram. Int. 43 (2017) 12079-12088.
[68] P. Colomban, L. Arberet, B. Kirmizi, On-site Raman analysis of 17^{th} and 18^{th} century Limoges enamels: Implications on the European cobalt sources and the technological relationships between Limoges and Chinese enamels, Ceram. Int. 43 (2017) 10158-10165.
[69] B. Gratuze, I. Soulier, M. Blet, L. Vallauri, De l'origine du cobalt: du verre à la céramique, Revue d'Archéométrie 20 (1996) 77-94.
[70] A. Zucchiatti, A. Bouquillon, I. Katona, A. D'Alessandro, The 'Della Robbia blue': a case study for the use of cobalt pigments in ceramics during the Italian renaissance, Archaeometry 48 (2006) 131-152.
[71] P. Colomban, G. Sagon, X. Faurel, Differentiation of antique ceramics from the Raman spectra of their coloured glazes and paintings, J. Raman Spectrosc. 32 (2001) 351-360.
[72] L.D. Knock, D. De Waal, Raman analysis of ancient pigments on a tile from the Citadel of Algiers, Spectrochim. Acta A 71 (2008) 1348-1354.
[73] F. Rosi, V. Manuali, T. Grygar, P. Bezdicka, B.G. Brunetti, A. Sgamellotti, L. Burgio, C. Seccaroni, C. Miliani, Raman scattering features of lead pyroantimonate

compunds: implication for the non-invasive identification of yellow pigments on the ancient ceramics. Part II. *In situ* characterisation of Renaissance plates by protable micro-Raman and XRF studies, J. Raman Spectrosc. 42 (2011) 407-414.
[74] L. Cartechini, F. Rosi, C. Miliani, F. D'Acapito, B.G. Brunetti, A. Sgamellotti, Modified Naples yellow in Renaissance majolica: study of Pb-Sb-Zn and Pb-Sb-Fe ternary pyroantimonates by X-ray absorption spectroscopy, J. Anal. At. Spectrom. 26 (2011) 2500-2507.
[75] V. Tanevska, Ph. Colomban, B. Minčeva-Šukarova, O. Grupče, Characterization of pottery from the Republic of Macedonia I: Raman analyses of Byzantine glazed pottery excavated from Prilep and Skopje (12^{th}-14^{th} century), J. Raman Spectrosc. 40(9) (2009) 1240-1248.
[76] J.W. Lewis, J.L. Payne, I. Radosavljevic Evans, H.T. Stokes, B.J. Campbell, J.S.O. Evans, An Exhaustive Symmetry Approach to Structure Determination: Phase Transitions in $Bi_2Sn_2O_7$, J. Amer. Chem. Soc. 138 (25) (2016) 8031–8042.
[77] C. Sandalinas, S. Ruiz-Moreno, A. López-Gil, J. Miralles, Experimental confirmation by Raman Spectroscopy of Pb-Sn-Sb triple oxide yellow pigment in sixteenth-century Italian pottery, J. Raman Spectrosc. 37 (2006) 1146-1153.
[78] S. Ruiz-Moreno, C. Sandalinas, R. Pérez-Pueyo, A. Gabaldón, M.J. Soneira, Raman laser fibre optic strategy for non-destructive pigment analysis. Identification of a new yellow pigment (Pb, Sn, Sb) from the Italian XVII century painting**,** J. Cult. Herit. 4 (2003) 309-313.

Figure Captions:

Fig. 1. Early modern painted pottery from the Belgrade fortress: Malhornware (BF I, BF II) and Anabaptist faience (BF III).

Fig. 2. BF I group of samples.

Fig. 3. BF II group of samples.

Fig. 4. BF III group of samples.

Fig. 5. Cross sections of typical samples from investigated groups: a) BF I-1; b) BF I-13; c) BF II-8; d) BF II-11; e) BF III-1; f) BF III-2.

Fig. 6. PXRD patterns and the Rietveld fits obtained for representative BF I and BF III samples. Red curves are the calculated patterns, differently coloured curves are the observed patterns and the difference curves are shown in grey.

Fig. 7. FTIR spectra of representative samples from three BF groups of pottery; abbreviations: Q-quartz; Cal-calcite, Si-O stretches (originated from aluminoslicates).

Fig. 8. Scatter plots of the pEDXRF data for ceramic assemblage excavated at Belgrade fortress. a) Scatter plot of the first three principal components of the EDXRF dataset; b) Scatter and loadings plot of PC1 and PC3 of the selected variables.

Fig. 9. Scattering matrix based dimension reduction. Features 1 and 2 represent newly formed variables.

Fig. 10. Raman spectra of: a) the light brown pigmented area of sample BF I-9; b) blue pigmented area of sample BF III-5; abbreviations: He-hematite, M-magnetite, LAs-lead-arsenate, Q-quartz.

Fig. 11. Raman spectrum of the yellow pigmented area of sample BF III-7; abbreviations: TLA- pyrochlore structure of Sn-containing lead(II) antimonate ($Pb_2Sb_{2-x}Sn_xO_{7-x/2}$), R-rosiaite ($PbSb_2O_6$).